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19. ABSTRACT (Continue on reverse if necessary and identify by block number)  Four experimental studies were performed in the previous period: Effect of protein adsorption on capacitance of water/nitrobenzene interface, Potentiometric study of fluorescent oxacyanine cation partitioning, frozen interfaces and microinterfaces. The most valuable experimental technique in use is impedance spectroscopy in the frequency range from 1 Hz to 65 kHz. Currently a new nonlinear least square software for data evaluation is being utilized.  In the study of oxacyanine dyes, both experimental and computational potentiometry were used. The results provided more insight in interfacial potential behavior. The contribution was particularly significant in providing large set of data previously unpublished.  Liquid/liquid microinterface is in its initial stage of investigation. The phenomenon similar to "microelectrodes" is clearly present, current work is aimed at reproducibility. Similarly, the concept of frozen interface is nearing first publishable stage.			
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Petr Vanýsek  
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## INTRODUCTION

Interface arising at the contact between two immiscible electrolytes is of fundamental interest to electrochemistry in basic research as well as to scientists in applied fields, namely to analytical chemists developing new sensors. The interface also has, however, a significant potential in relation to the studies on membrane models.

Primarily, an interface between immiscible oil/water phase, can be visualized as one "layer" of the "double-layer" biological membrane. (Figure 1). A sophisticated, well conceived experiment can thus be designed to further knowledge about processes on biological membranes.

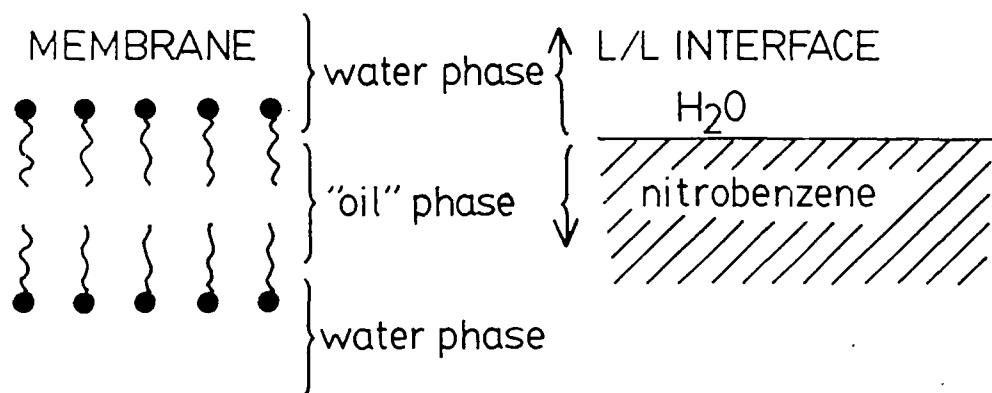


Figure 1

## RESEARCH OBJECTIVES

Various electrochemical methods, including hybrid electrochemical optical techniques allow us to study kinetics on the interface, adsorption processes, transfer across the interface and the structure of the interfacial double layer.

The results are then in turn extrapolated and applied to the behavior on more complicated structures such as membranes. In this project, the following problems are especially investigated:

- ▶ The effects of biologically active materials on simple ion transfer kinetics
- ▶ Potential sensitive fluorescence dyes in liquid/liquid electrochemistry
- ▶ Properties of a microinterface formed between two immiscible electrolytes.

## PROGRESS DURING LAST YEAR

### 1. Effect of protein adsorption on impedance of water/nitrobenzene interface.

A solvent system used in our experiment was water/nitrobenzene, with LiCl as a supporting electrolyte for aqueous phase and tetrabutylammonium tetraphenylborate (TBATPB) as a supporting electrolyte for the nonaqueous phase. The concentrations used were between 0.02 and 0.1 mol/l, same in both solvents. An impedance of the system was measured between 1 Hz and 65 kHz, with 12 data points per frequency decade.

A water soluble protein bovine serum albumin (BSA) has been added to aqueous phase to study its adsorption effect on the liquid/liquid interface. The impedance measurements were performed at the analytical concentration of the protein in the aqueous phase (discounting adsorption) between 0.5 to 100 ppm, with particular emphasis on lower concentrations. The reason for that is, that the results at the low concentrations show nonmonotonous impedance as a function of protein concentration.

In particular, a local minimum in impedance (corresponding to maximum capacitance) is observed around 5 ppm of protein. This concentration corresponds to a monolayer formation at the interface. Bias DC potential of different values was applied on the interface while measuring impedance properties of the system to obtain information on potential of zero charge. The results are qualitatively similar to the findings of Wandlowski et al. ( T. Wandlowski, S. Račinský, V. Mareček and Z. Samec, J. Electroanal. Chem. 227, 281 (1987); T. Wandlowski, V. Mareček and Z. Samec, J. Electroanal. Chem. 242, 277 (1988)), who performed similar types of measurements on phosphatidylcholine adsorption. Their interpretation of data seems to be, however, incorrect (a frequency dependent capacitance), thus we are currently working on an impedance model that will enable rigorous interpretation of our impedance data as well as the data reported by Wandlowski et al. An effort to determine appropriate equivalent circuit wiring using a newly acquired software is under way.

### 2. Potentiometric investigation of fluorescent dye partitioning between two immiscible liquids.

The study has provided a complete information on potential response of a liquid/liquid interface with base electrolytes in the presence of oxacyanine dye cation over several orders of magnitude in the dye concentration and water/solvent volume ratio. The work which originally started as a study of the dye applicability in fluorescence indication of potential differences yielded results (both theoretical and experimental) applicable to any potentiometric study on liquid/liquid interface. In particular, the computer simulation explains super-nernstian response of the system, which is sometimes observed experimentally; a phenomenon not entirely obvious to a

casual observer. From the partition coefficient measurements thermodynamic data (Gibbs energies of transfer) were obtained for a series of the dyes.

In potentiometric measurements on liquid/liquid interface it is quite usual to assume just a simple relationship between potential and activity of electroactive species  $i$  which partitions between the two phases.

$$E = E^\circ + \frac{RT}{nF} \ln a_i \quad (1)$$

It is often assumed that the prerequisites for other ions not to participate in the potential determining equilibrium are fulfilled. It seems, however, that in reality this is not always the case. We have shown both experimentally and through a numerical model that other factors such as base electrolyte concentrations, volumes of the two phases and impurities influence the potential.

The effects are best depicted in three-dimensional plots. Figure 2 shows calculated effect of the water/nonaqueous solvent ratio on potential of an interface containing an oxacyanine cation. All calculations were based on a system containing 0.01 mol/l LiCl in water and tetrabutylammonium tetraphenylborate in nitrobenzene.

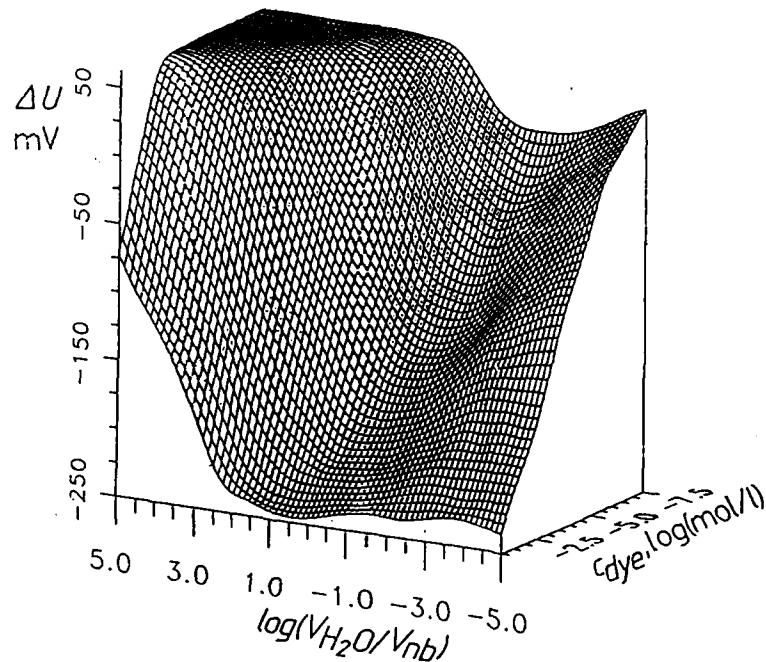


Figure 2

Theoretical effect of the water/nitrobenzene volume ratio on the potential - dye concentration relationship. The axes are x: logarithm of  $\text{DiOC}_1(3)$  concentration; y: logarithm of ratio of water volume to nitrobenzene volume; z: calculated interfacial potential.

In the range of the dye ion concentrations from  $10^{-3}$  to  $10^{-5}$  mol/l and roughly 1:1 volume ratio (a typical experimental situation), the slope of potential vs.

logarithm of concentration is 55 mV/decade. This linear value is different from the intuitively expected and by equation (1) predicted 59 mV. This difference is easy to understand, though. An increase in concentration in one phase will be followed by a subsequent repartitioning of all the ions present. Since repartitioning is aiding the interfacial potential to maintain the interfacial equilibriums, less than the 59 mV change is needed.

Figure 3 shows the effect of an impurity in the system on the potential of a system described previously (Figure 2). Impurity of the chosen properties (potential of transfer -100 mV for cation, +100 mV for anion) has little effect except at dye concentrations below  $10^{-5}$  mol/l and water/nitrobenzene ratio between 0.1 and 100.

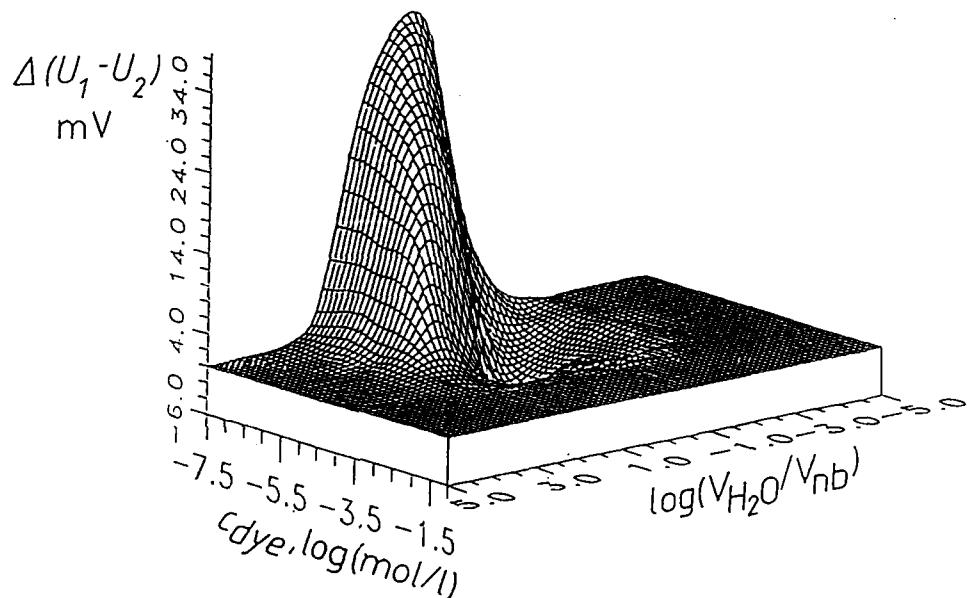


Figure 3

Influence of an electroactive impurity on the slope of the potential - dye concentration curve. z: difference between interfacial potential with and without an impurity.

Repeated calculations with other parameters make it possible to calculate effects of other known or assumed impurities and also known to be present, but quite often neglected, ions such as  $H^+$  from water. Calculations and experiments show that pH will not affect the potential measurement if the pH is between 4-7. This is an important finding as the use of any buffer is usually undesirable since it complicates the partition on the interface.

### 3. Frozen Interface

A new system consisting of a cooled system in which one of the phases becomes solid has been tested. The goal of the experiment is to compare the response

of a liquid/liquid system and a liquid/ice system and from the difference in the data (impedance, cyclic voltammetry) separate the interfacial property of the two adjacent double-layers. Frozen electrolytes retain enough conductivity to allow impedance measurements, although cyclic voltammetry on the system is difficult to perform. The problem is in the low compliance voltage of the potentiostat, which often reaches saturation. Thus, the impedance spectroscopy studies are very suitable for our purpose. The newly acquired impedance analysis software is currently being applied for this study as well.

#### 4. Microinterface

Experiment aimed towards utilization of a small interface (as in the tip of a capillary) are currently under way. The findings show that a small size liquid/liquid interface can be formed and subsequently studied by the techniques applicable to "ultra-micro-electrodes" ( $\leq 25 \mu\text{m}$  diameter). The main obstacle in the present work is a lack of reproducibility. It is clearly traceable to a position of the interface within the capillary but the position, being potential dependent, is difficult to maintain. The ultimate goal of this work will be to develop a technique for the modeling of membrane channels.

In addition to a single micro-interface, an ensemble of such interfaces is studied on a Nuclepore membrane. One advantage is to be able to deal with relatively short pores, given by a thickness of the film, which is much smaller than the channel afforded through pulling of a capillary in flame. Two measuring techniques are being used for the system evaluation — impedance measurements and cyclic voltammetry of the membrane or microinterface.

#### PUBLICATIONS

- D. H. Wiegand and P. Vanýsek:  
Spectroscopic and fluorometric characterization of oxacyanine dyes in water and nitrobenzene. *Applied Spectroscopy*, **42**, 958, (1988)
- D. H. Wiegand and P. Vanýsek:  
Potentiometric studies of oxacyanine dyes on L/L interfaces, *J. Electroanal. Chem.*, Submitted
- D. H. Wiegand and P. Vanýsek:  
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- P. Vanýsek:  
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- I. C. Hernandez and P. Vanýsek:  
Supporting electrolyte for liquid/liquid interface: Crystal violet Tetraphenylborate, *Electrochim. Acta*, Submitted.

## ABSTRACTS:

P. Vanýsek:

Impedance studies on a (frozen electrolyte)/(liquid electrolyte) interface. Atlanta Electrochemical Society Meeting May 1988

D. H. Wiegand and P. Vanýsek:

Electrochemistry of oxacyanine dyes: Potentiometry on liquid/liquid interface. Atlanta Electrochemical Society Meeting May 1988.

## **TRAINING:**

Two graduate students were supported during the year.



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